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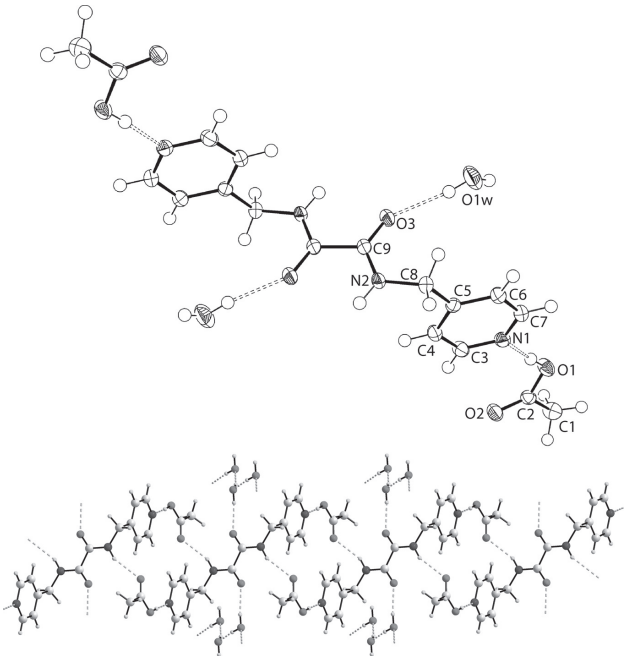
Crystal structure of the 1:2 co-crystal between *N*, *N′*-bis(4-pyridylmethyl)oxalamide and acetic acid as a dihydrate, $C_{14}H_{14}N_4O_2{\cdot}2\ C_2H_4O_2{\cdot}2\ H_2O$



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Abstract

$C_{18}H_{26}N_4O_8$, triclinic, $P\bar{1}$ (no. 2), $a = 4.7975(2)$ Å, $b = 9.8725(3)$ Å, $c = 11.0244(3)$ Å, $\alpha = 85.312(3)°$, $\beta = 79.872(3)°$, $\gamma = 87.600(3)°$, $V = 512.09(3)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0381$, $wR_{ref}(F^2) = 0.1064$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.13 × 0.08 × 0.06 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	0.93 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	76.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12778, 2132, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2064
$N(param)_{refined}$:	152
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

N,*N′*-Bis(pyridin-4-ylmethyl)oxalamide, $^4LH_2$, was prepared according to the literature procedure [5] (melting point, m.pt: 485–486 K; lit. [5]: 486–487 K). The title co-crystal solvate was prepared by dissolving $^4LH_2$ (0.154 g, 1 mmol) in an excess of glacial acetic acid (3 mL). Upon dissolution, benzene (3 mL) was carefully layered on top of the solution. Colourless crystals formed approximately one week after the crystallisation and shown crystallographically to be $^4LH_2{\cdot}2CH_3C(=O)OH{\cdot}2H_2O$. **M.pt**: 374–376 K. **IR** (ATR, cm^{-1}): 3278(s) ν(N—H), 3168–2919(w) ν(C—H), 1710–1649(s) ν(C=O), 1524(s) ν(C=C), 1357(m) ν(C—N), 710(s) δ(C=C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The O- and N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraints of O—H = 0.84±0.01 Å and N—H = 0.88±0.01 Å, respectively, and with $U_{iso}(H)$ set to $1.5U_{equiv}(O)$ and $1.2U_{equiv}(N)$, respectively. One of the water-bound hydrogen atoms was statistically disordered over two sites. Difference

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
O1	−0.0316(2)	0.67171(9)	0.39091(9)	0.0215(2)
H1O	0.069(4)	0.691(2)	0.4434(15)	0.032*
O2	0.0344(2)	0.88746(9)	0.31598(9)	0.0208(2)
C1	−0.2532(3)	0.74917(15)	0.22251(13)	0.0221(3)
H1A	−0.450952	0.771851	0.256332	0.033*
H1B	−0.235150	0.652773	0.206326	0.033*
H1C	−0.194254	0.804918	0.145236	0.033*
C2	−0.0687(3)	0.77664(13)	0.31375(12)	0.0161(3)
O3	0.32813(19)	0.84427(9)	1.01777(8)	0.0177(2)
N1	0.2813(2)	0.71711(11)	0.55318(10)	0.0173(2)
N2	0.7261(2)	0.91165(10)	0.88469(10)	0.0144(2)
H2N	0.823(3)	0.9833(13)	0.8508(14)	0.017*
C3	0.3408(3)	0.84326(13)	0.57505(12)	0.0178(3)
H3	0.270665	0.917899	0.528072	0.021*
C4	0.5003(3)	0.86942(13)	0.66329(12)	0.0168(3)
H4	0.537781	0.960303	0.676473	0.020*
C5	0.6050(3)	0.76099(12)	0.73235(11)	0.0139(3)
C6	0.5454(3)	0.62963(13)	0.70875(12)	0.0170(3)
H6	0.615620	0.553051	0.753320	0.020*
C7	0.3828(3)	0.61228(13)	0.61955(12)	0.0184(3)
H7	0.341175	0.522509	0.604633	0.022*
C8	0.7810(3)	0.78179(12)	0.83007(12)	0.0152(3)
H8A	0.743413	0.707725	0.896466	0.018*
H8B	0.983935	0.774863	0.792744	0.018*
C9	0.5066(3)	0.92940(12)	0.97453(11)	0.0132(3)
O1W	0.2347(3)	0.55775(10)	1.03265(11)	0.0319(3)
H1W	0.244(5)	0.6434(10)	1.020(2)	0.048*
H2W[a]	0.103(6)	0.530(3)	1.000(4)	0.048*
H3W[a]	0.390(4)	0.522(3)	1.000(4)	0.048*

[a]Occupancy: 0.5.

Fourier maps appear to indicate partial proton transfer to give a pyridinium cation and acetate anion in a ca. 0.3 : 0.7 ratio. On the basis of the great disparity in the C2—O1, O2 bond lengths (see below) the molecules were modelled as neutral. Further multi-temperature experiments would clarify whether proton transfer occurs as a function of temperature or whether the above observation is an artefact of the data.

Comment

The structural chemistry of isomeric molecules of the general formula (n-C_5H_4N)$CH_2N(H)C(=O)C(=O)N(H)CH_2$($C_5H_4$N-n), for n = 2, 3 and 4, abbreviated as $^nLH_2$, and their co-crystals, salts and metal complexes has been reviewed recently [6]. The key feature of the molecules in terms of co-crystal formation is the presence of a central di-amide functionality as well as two terminal pyridyl residues, both of which are capable of participating in conventional hydrogen bonding. Continuing interest in examining co-crystal formation of $^4LH_2$ and their ability to generate coordination polymers [7–9], lead to the isolation of the title 2:1 co-crystal di-hydrate, $^4LH_2{\cdot}2CH_3C(=O)OH{\cdot}2H_2O$.

The molecular structure of the constituents of the crystal are shown in the figure (70% displacement ellipsoids; the full molecule of $^4LH_2$ and symmetry-related acetic acid and water molecules are generated by the symmetry-operation (i) $1-x$, $2-y$, $2-z$; in the Figure the water is shown as ordered). The $^4LH_2$ molecule is disposed about a centre of inversion so the pyridyl rings adopt an anti-periplanar disposition. The central $C_2N_2O_2$ atoms are co-planar [r.m.s. deviation = 0.0034 Å], with the adjacent C8 atoms lying 0.065(2) Å to either side of the plane. An intramolecular amide-N—H···O(amide) hydrogen bond is noted [N2—H2n···O3^i: H2n···O3^i = 2.335(14) Å, N2···O3^i = 2.7025(13) Å, with angle at H2n = 105.1(11)°] which gives rise to an $S(5)$ loop using graph-set notation [10]. An orthogonal relationship between the central plane and each terminal pyridyl ring is evident as seen in the dihedral angle between the planes of 87.28(3)°. Suggestive evidence that the carboxylic acid is just that, an acid, is found in the great disparity in the C2—O1, O2 bond lengths of 1.3122(16) and 1.2232(16) Å, respectively; see Experimental details for the possibility of partial proton transfer.

Significant hydrogen bonding is evident in the molecular packing. As seen from the figure, there are acetic acid-O—H···N(pyridyl) [O1—H1o···N1: H1o···N1 = 1.754(18) Å, O1···N1 = 2.6051(14) Å with angle at H1o = 175.6(19)°] and water-O—H···O(amide) [O1w—H1w···O3: H1w···O3 = 2.038(11) Å, O1w···O3 = 2.8694(14) Å with angle at H1w = 167(2)°] hydrogen bonds. The aforementioned hydrogen bonds give rise to a five-molecule aggregate. In the crystal, the acetic acid-O—H···N(pyridyl), mentioned above, combine with amide-N—H···O(carbonyl-acetic acid) hydrogen bonds [N2—H2n···O2^{ii}: H2n···O2^{ii} = 2.174(15) Å, N2···O2^{ii} = 2.9542(14) Å with angle at H2n = 147.2(13)° for (iii) $1-x$, $2-y$, $1-z$] to give rise to 22-membered, centrosymmetric $\{\cdots HNC_4N\cdots OHCO\}_2$ synthons and supramolecular tapes along the c-axis direction. The water molecules are connected to the chains laterally (along the b-axis direction) and are linked to each other normal to the tapes via water-O—H···O(water) hydrogen bonds to form chains along the a-axis and therefore, stabilise a three-dimensional architecture. As noted in the Experimental details, the second water-bound hydrogen atom is disordered over two positions, in a 50:50 ratio for H2w and H3w, and so there are two such connections to consider [O1w—H2w···O1w^{iii}: H2w···O1w^{iii} = 1.97(3) Å, O1w···O1w^{iii} = 2.7945(19) Å with angle at H2w = 165(4)° and O1w—H3w···O1w^{iv}: H3w···O1w^{iv} = 1.92(2) Å, O1w···O1w^{iv} = 2.7468(19) Å with angle at H3w = 165(4)° for (iii) −x, 1 − y, 2 − z and (iv) $1-x$, $1-y$, $2-z$]. In order to gain further insight into the

supramolecular association in the crystal, Crystal Explorer 17 [11] was employed to calculate the Hirshfeld surfaces as well as the full and delineated two-dimensional fingerprint plots which was analysed following established procedures [12]. Initially, the calculations were performed on the five-molecule aggregate illustrated in the upper view of the figure; the reported values are the average of the results calculated for the individual disorder components. The most important contribution to the Hirshfeld surface comes from H···H contacts [40.6%]. However, O···H/H···O contacts make a notable contribution to the calculated surface, at 35.5%, which is consistent with the significant H···O contacts identified above. The other major contribution comes from C···H/H···C contacts [15.1%]. Other contributions >2% to the surface are due to N···H/H···N [3.2%] and O···O [1.6%]. Very similar percentage contributions are noted in a closely related structure, $^3LH_2{\cdot}2CH_3C(=O)OH$ [13], that is with the isomeric 3-pyridyl base and lacking solvent water molecules. Hence, in this latter structure, H···H and O···H/H···O contacts are calculated to contribute 44.1 and 30.0%, respectively, to the overall surface. Contacts of the type C···H/H···C [14.4%] also make a significant contribution, followed by N···H/H···N [4.7%] and O···C/C···O [3.2%] but at long separations. Calculations were also performed on the individual $^4LH_2$ and acid molecules. For the former, the major contributions to the calculated Hirshfeld surface were H···H [38.7%], O···H/H···O [28.5%], C···H/H···C [19.1%] and N···H/H···N [9.4%], together contributing to over 95% of all contacts to the overall surface. The remaining contacts are O···N/N···O [1.5%], N···C/C···N [1.1%], O···C/C···O [1.0%] and C···C [0.7%]. For the molecule of acetic acid, hydrogen atoms are involved in over 96% of all surface contacts: O···H/H···O [41.4%], H···H [38.4%], N···H/H···N [8.5%] and C···H/H···C [8.0%].

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